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MERCURY IN FISH FROM THE NARROWS IN PARLBY CREEK-BUFFALO LAKE

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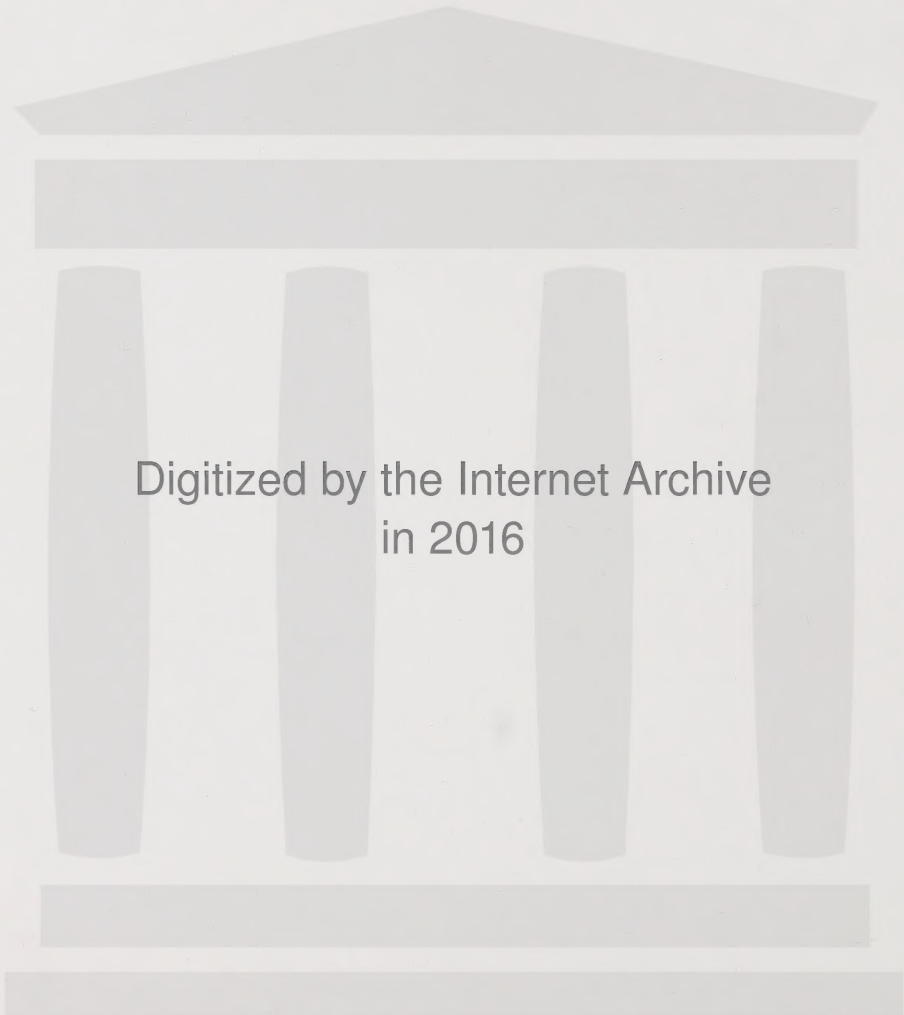

MERCURY IN FISH FROM THE NARROWS IN PARLBY CREEK-BUFFALO LAKE

by

S. Wu, Ph.D.
Y. Zhao, B.Sc.
D. Lucyk, B.Sc.
F.P. Dieken, Ph.D.

Environmental Chemistry
Alberta Environmental Centre

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ACKNOWLEDGEMENTS

Sampling and fish age determinations performed by personnel from Fisheries Management Section of Alberta Fish and Wildlife, Central Region, Red Deer are greatly appreciated.

SUMMARY

Mercury analysis of fish collected from "The Narrows" in Parlby Creek-Buffalo Lake was conducted in June 1993. Of the 15 northern pike (*Esox lucius*), 3 longnose sucker (*Catostomus catostomus*) and 1 white sucker (*Catostoms commersoni*) collected, none contained mercury levels exceeding the 0.5 mg kg^{-1} Canadian Federal Guideline for commercially-marketed fish. The range of total mercury concentrations in fish muscle tissue (based on wet weight) was 0.077 to 0.269 mg kg^{-1} with a mean value of 0.150 mg kg^{-1}. Regression analysis for northern pike revealed that fork length, age and weight linearly correlated with total mercury concentration with r^2 values of 0.45, 0.46 and 0.34, respectively. The mean mercury level of northern pike sampled in this study is considered similar to, or lower than, that sampled in 1983-1985 in nearby Pine Lake, Red Deer River, and Gleniffer Lake.

1 INTRODUCTION

The Parlby Creek-Buffalo Lake Water Management Project is an ongoing project started in 1985 by Alberta Environment (now Alberta Environmental Protection). The project objectives include controlling flooding of agricultural lands, enhancing fish and wildlife habitat, securing municipal water supply and stabilizing water levels in Buffalo Lake for recreational purposes. The proposed lake stabilization component of this project involves diverting water from the Red Deer River, increasing flow through Parlby Creek, and raising the current level of the lake to maintain an elevation between 780.5 and 781.0 m (Environmental Management Associates, 1991).

This project has caused concern regarding the elevation of mercury levels in fish tissue. Raising the water level of a lake or increasing the flow of a creek could increase the methylation rate of mercury in the aquatic system, by increased activities of methylating bacteria and other microorganisms in freshly-inundated or eroded soil. Since organisms tend to accumulate methylated mercury efficiently, mercury levels in fish tissue and other aquatic species may increase. Increased mercury levels in fish have been reported in several impoundments in Canada and elsewhere (Jackson et al., 1991; Jackson, 1991; Green, 1990; Bodaly et al., 1984; Abernathy and Cumbie, 1977). However, based upon a five-year study, elevation of mercury levels did not occur in the newly-formed Dickson Dam Reservoir (Gleniffer Lake) in Alberta (Alberta Environmental Centre, 1989). In addition, mercury concentrations in water close to or exceeding the Freshwater Aquatic Life Canadian Water Quality Guideline of 0.1 µg/L were observed occasionally in the Red Deer River but not in Buffalo Lake and Parlby Creek.

To allow future evaluation of the impact of the Parlby Creek-Buffalo Lake Water Management Project on the aquatic system, background information on mercury levels in fish muscle tissue was required. The Water Analysis Laboratory (WAL) at the Alberta Environmental Centre (AEC) was contracted by the Buffalo Lake Management Team, Alberta Environment Protection, to provide fish mercury analysis and data interpretation.

It was agreed that sampling would be performed at "The Narrows" by personnel from the Fisheries Management Section of Alberta Fish and Wildlife, Central Region, Red Deer. The Narrows is a popular angling site located at the west side of Buffalo Lake, connecting Hindleg Bay and Parlby Bay (the outlet of Parlby Creek) (Fig. 1). It is known that northern pike (*Esox lucius*), burbot (*Lota lota*), longnose sucker (*Catostomus catostomus*) and white sucker

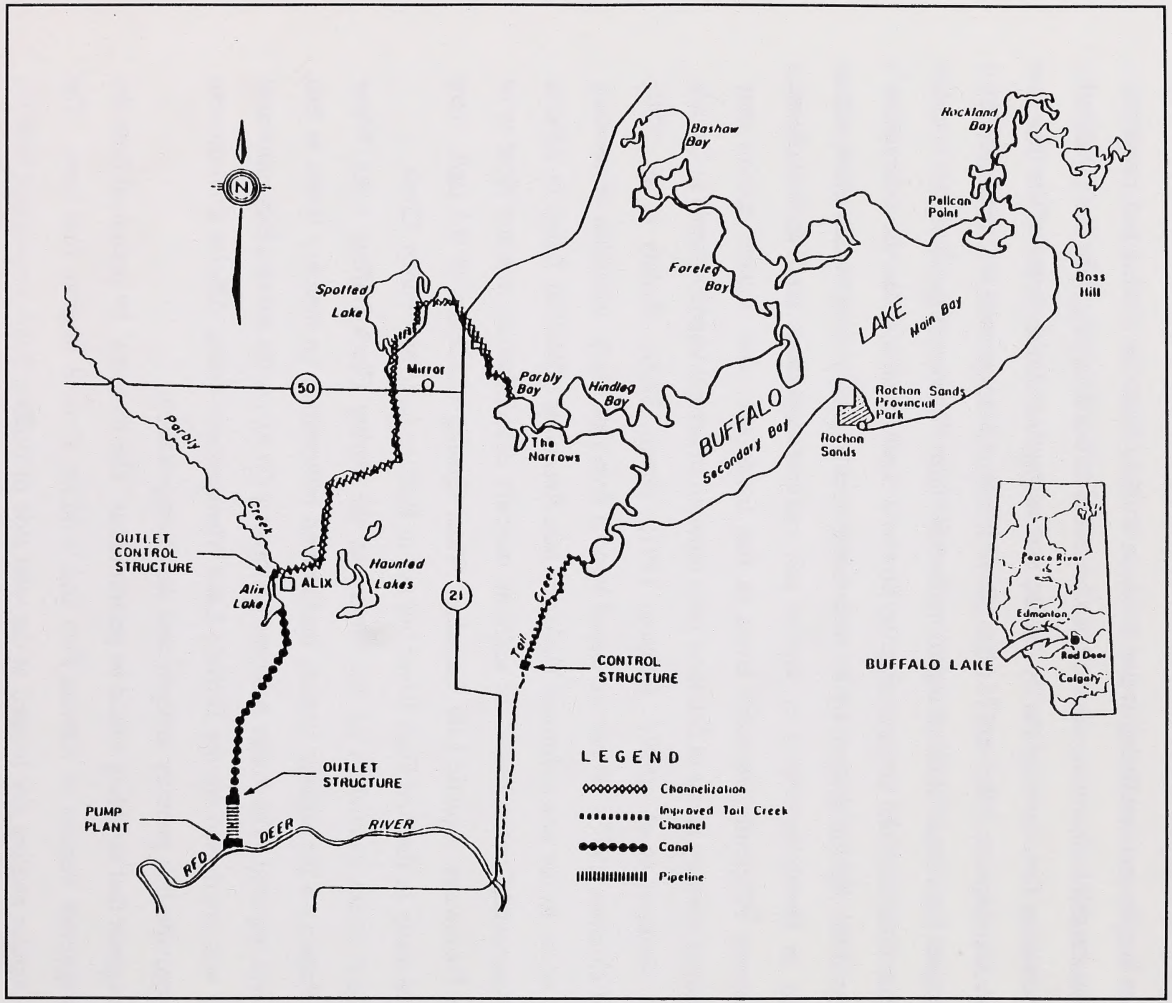


Figure 1. Parlby Creek-Buffalo Lake Water Management Project Layout (taken from Fig. 2 in Environmental Management Associates, 1991)

(*Catostomus commersoni*) traditionally inhabit The Narrows waterway. It was also agreed that the sample size would be 7-15 samples for each of the four species mentioned above. If additional species were captured, they would be selected for study.

2 GENERAL BACKGROUND ON MERCURY ACCUMULATION IN FISH

Mercury levels in fish are determined by a dynamic relationship between mercury uptake and clearance rates. Uptake rates are a function of the absorption of mercury directly from the water or indirectly via the food chain (Fagerstorm et al., 1974; Stokes and Wren, 1987). The relative importance of these two uptake processes has not been clearly established, even under laboratory conditions, and is probably species and site specific.

Characteristics of fish and the environment both influence mercury accumulation in fish. Fish characteristics include the level of the species in the aquatic food chain, food consumption rates, food conversion efficiencies, growth rates, mercury elimination rates and the efficiency of mercury uptake (Stokes and Wren, 1987; Mathers and Johansen, 1985).

Environmental characteristics include water temperature, general trophic or nutrient conditions, as well as water and sediment chemistry (Reinert et. al., 1974; Bodaly et. al., 1986, Wright and Hamilton, 1982; Rudd and Turner, 1983; Jackson, 1991). Among the water and sediment chemistry factors which are particularly important in determining mercury uptake, the concentration of mercury and bioavailable mercury (mainly methylmercury) in water and sediment, pH, concentration of dissolved calcium, redox potential of sediment, oxygen content, quantity and type of suspended and sedimentary Hg-binding substances such as organic matter, clay minerals, hydrous Mn and Fe oxides, sulphide and selenium, etc. are the key factors (Jackson et. al., 1991; Grieb et. al., 1990; Jackson, 1988; Wren and MacCrimmon, 1983; Rodgers and Beamish, 1983; Speyer, 1980). The higher the amounts of sulphide, selenium and hydrous Mn and Fe oxides in sediments and the higher the redox potential, the lower the amount of easily solubilized, exchangeable forms of inorganic mercury existing in the sediment, and hence, the lower are the methylmercury levels in bottom sediments and the water column. Also, higher temperatures, pH ranges of 6.0-7.5, and a combination of adequate oxygen amount with large, but suitable, amounts of organic matter may favour a higher microbial methylation/demethylation ratio from water and/or sediments. Nevertheless, methylation occurs within a wide range of

trophic conditions, redox potentials and pH, indicating that methylation is carried out by different kinds of microbes, each differing in its ecological requirements (Environment Canada, Manitoba, 1987; Jackson, 1991).

3 CONDUCT OF THE STUDY

3.1 Sampling

Sampling was conducted on June 14, 1993 at The Narrows by personnel from the Fisheries Management Section of Alberta Fish and Wildlife, Central Region, Red Deer, while performing netting tests.

One gang of gill nets totalling 229.5 metres in length were used. It consisted of 91.4 m of 6.4 cm stretched mesh, 91.4 m of 8.9 cm stretched mesh and 46.7 m of 11.4 cm stretched mesh set at 10:00 hrs and lifted at 12:00 hrs and 14:00 hr. Fifteen northern pike, one white sucker and three longnose sucker were captured and retained in coolers.

On the same day in the field laboratory, fork lengths and weights of all fish were measured. Field sample numbers were assigned to northern pike and sex was determined. The cleithra were removed from northern pike for aging purposes. All of the fish were stored in plastic bags, 4 or 5 fish per bag, and frozen at -20°C within five hours of capture. The next day the frozen fish were packed in ice in a cooler and sent to AEC; they were received that same day.

At AEC, the fish were kept frozen at -20°C. They were taken out for thawing 16 hrs before fileting. Fileting was performed according to documented procedures (Water Analysis Laboratory, 1993). Before fileting, the fish fork length and weight were measured and recorded. Fish muscle tissue taken from the front, left side of each fish was analyzed for mercury content.

3.2 Analysis for Total Mercury

To determine total mercury in fish tissue the sample is digested with a mixture of sulphuric and nitric acids to solublize the tissue and to oxidize all forms of mercury in the biological tissue to its divalent ionic form. Mercury ions (Hg^{2+}) are then reduced by stannous

chloride solution to their elemental form (Hg°), determined by the traditional cold vapour atomic absorption spectrometry (Water Analysis Laboratory, 1993).

3.3 Quality Control of Mercury Analyses

Analytical data quality was controlled using established protocols which are summarized below.

An analytical system is defined as the combined contributions of the instrument, established and documented method, and analyst. For fish mercury determination, analytical system performance is monitored by including four types of Quality Control (QC) samples with each batch of test samples:

I. QC standard solutions QCA(ℓ), QCB(ℓ) and QCBLK(ℓ) with known mercury concentrations to evaluate the accuracy and precision of the analytical system for standard solutions, where (ℓ) denotes liquid.

II. In-house prepared defatted dry QC fish samples QCA(s) and QCB(s) to evaluate relative accuracy and precision of the analytical system for fish samples, where (s) denotes solid.

III. Certified Reference Material (CRM) DORM-1, (dried dogfish muscle tissue) obtained from the National Research Council of Canada, to evaluate the accuracy of the analytical system for a CRM fish sample.

IV. Three randomly selected duplicate sub-samples of fish tissue in each batch of analyses to evaluate the precision of the analytical system for fish samples.

The analytical results for the QC Samples are compared to the design values, historical means, or certified values, as appropriate, and expressed in terms of percentage recovery to evaluate the accuracy. The results of QCA, QCB, QCA+QCB, QCA-QCB, and the difference between the duplicates are statistically compared with the lower and/or upper warning and control limits derived from WAL's historical performance information on these materials at the 95% and 99% confidence level, respectively.

An analysis is considered unacceptable if any QC result exceeds the lower or upper control limits. An out-of-control result of QCA+QCB indicates the existence of systematic error in the analytical system. An out-of-control result of QCA-QCB indicates poor precision. If the

difference between the duplicate results exceeds the control limit, the reproducibility of the analytical procedure is in question. If the QC samples indicate the analytical system is out-of-control, all of the fish tissue analyses for that run/batch are repeated, after the cause of the system failure is identified and corrected.

The quality control results observed during analyses of fish from The Narrows are presented in Table 1. All QC data are within the prescribed corresponding control limits. The recoveries of QC samples are within 97-104%. The recovery of CRM DORM-1 is 97%. These data demonstrate the acceptable performance of the analytical mercury measurement system, and consequently the quality of the fish mercury concentration results reported in this study are judged to be satisfactory.

4 RESULTS

Summarized and individual fish mercury results are presented in Table 2 and Appendix A, respectively. None of the fish sampled at The Narrows from Parlby Creek-Buffalo Lake contained a total mercury concentration exceeding the 0.5 mg kg^{-1} Canadian Federal Guideline for commercially-consumable fish (Health and Welfare Canada, 1990). The concentration range of total mercury is 0.077 - 0.269 mg kg^{-1} with a mean value of 0.15 mg kg^{-1} for all fish species.

Regression analyses of total mercury concentration in northern pike versus field fork length, age and weight, Fig. 2, indicate significant correlations with r^2 values of 0.45, 0.46, and 0.34, respectively.

5 DISCUSSION

The major fish species sampled in this study is northern pike. Northern pike is a piscivorous species at the top of the food chain. Laboratory experimental studies, conducted at 18°C, have shown that northern pike assimilate about 20% of the mercury contained in prey fish which they ingest (Phillips and Gregory, 1979). The half-life of mercury in northern pike may be as long as two years (Lockhart et al., 1972; Uthe, 1972). The correlation of mercury content in northern pike with changes in environmental factors has been reported as being relatively poor (Jackson, 1991). Since it is a popular species for sport fishing at The Narrows, monitoring mercury levels in northern pike is an important relevant human health protection measure.

Table 1. Quality control results for total mercury analyses

I. Quality Control Standard Solutions (µg per 25 mL)

Date	Sample Name*	Design Value	Warning Limit		Control Limit		Measured Value	% Recovery	Acceptable
			Lower	Upper	Lower	Upper			
June 24, 93	QCA(ℓ)	0.375	0.361	0.389	0.355	0.396	0.375	100	yes
June 24, 93	QCB(ℓ)	0.125	0.116	0.134	0.112	0.138	0.130	104	yes
June 24, 93	QCBIK(ℓ)	0.000	-0.006	0.006	-0.009	0.0019	0.001	NA	yes
June 24, 93	QCA(ℓ)+QCB(ℓ)	0.500	0.481	0.519	0.471	0.529	0.505	101	yes
June 24, 93	QCA(ℓ)-QCB(ℓ)	0.250	0.237	0.263	0.231	0.269	0.245	98	yes

II. Quality Control In-House Defatted Dry Fish Samples (mg kg^{-1})

Date	Sample Name*	Historical		Warning Limit		Control Limit		Measured value	% Recovery	Acceptable
		Mean	n	Lower	Upper	Lower	Upper			
June 24, 93	QCA(s)	3.779	51	3.460	4.098	3.301	4.257	3.854	102	yes
June 24, 93	QCB(s)	1.392	48	1.284	1.520	1.225	1.579	1.414	102	yes
June 24, 93	QCA(s)+QCB(s)	5.162	48	4.777	5.580	4.577	5.781	5.260	103	yes
June 24, 93	QCA(s)-QCB(s)	2.376	48	2.115	2.635	1.985	2.765	2.440	103	yes

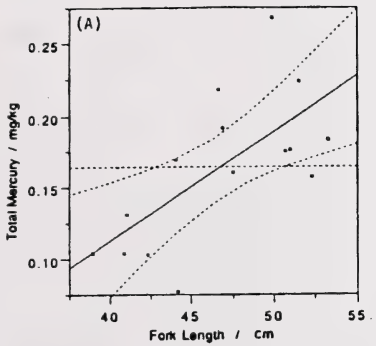
III. Certified Reference Material (mg kg^{-1})

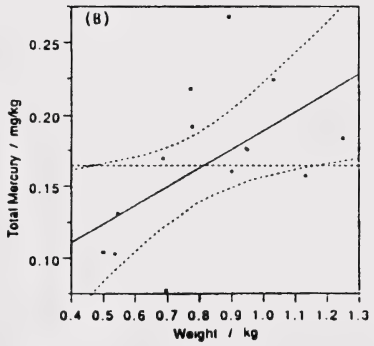
Date	Sample Name	Certified Value	Measured Value	% Recovery
June 24, 93	NRC DORM-1	0.798 ± 0.074	0.74	97

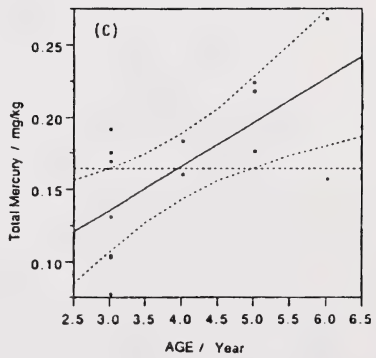
IV. Duplicates (mg kg^{-1})

Date	Sample #	Original	Duplicate	Difference			Acceptable
				Measured	Warning Limit	Control Limit	
June 24, 93	9303762	0.180	0.178	0.002	0.018	0.025	yes
June 24, 93	9303769	0.109	0.104	0.005	0.018	0.025	yes
June 24, 93	9303771	0.209	0.219	0.010	0.018	0.025	yes

* (ℓ) = liquid; (s) = solid







$Y = -0.1916 + 0.00762x$
$r^2 = 0.46$
$P < 0.0058$
$n = 15$

$Y = 0.05878 + 0.1304x$
$r^2 = 0.34$
$P < 0.022$
$n = 15$

$Y = 0.0445 + 0.03036x$
$r^2 = 0.46$
$P < 0.0057$
$n = 15$

Figure 2. Regression of total mercury levels in northern pike muscle tissue upon (A) fork length, (B) weight and (C) age. Horizontal lines represent the mean values. Solid lines represent the regression lines; dotted curves represent 95% confidence limits of the regression; symbols represent individual data points.

Table 2. Summary of total mercury concentrations in fish muscle tissue (wet weight) from The Narrows in Parlby Creek-Buffalo Lake in 1993

Species	Sample Size	Fork Length (cm)*		Weight (kg)*		Total Mercury (mg kg^{-1})	
		Mean	Range	Mean	Range	Mean	Range
Northern Pike	15	46.2	38.6-52.9	0.781	0.493-1.231	0.164	0.079-0.269
Longnose Sucker	3	41.2	40.8-41.7	1.044	0.997-1.100	0.104	0.089-0.114
White Sucker	1	35.5		0.676		0.077	
Overall	19	44.8	35.5-52.9	0.871	0.676-1.231	0.150	0.077-0.269

* Field measurements

For comparison purposes, fish mercury levels in the nearby Red Deer River below Dickson Dam and in nearby Pine Lake and Gleniffer Lake sampled in 1983 or 1984 (Alberta Environmental Centre, 1984; 1986) are summarized in Tables 3 and 4. In Table 5, mercury levels for northern pike from these sites are compared to those from The Narrows. The mean total mercury level of northern pike in this study was similar to that found 9 years ago in Pine Lake but lower than that found 9-10 years ago in the Red Deer River and Gleniffer Lake (Tables 3-5). It should be mentioned that fish mercury level determinations performed at or by the Alberta Environmental Centre during 1983-1985 were done using different methods in different laboratories.

The background mercury level identified in this study is significantly below the Canadian human health consumption guideline value of 0.5 mg kg^{-1} (Health and Welfare Canada, 1990). Full interpretation of the mercury level and its comparison with that in nearby aquatic systems measured 9-10 years ago (Table 5) would require further information on both fish and environmental characteristics as presented in section 2.

From a human health standpoint, organic mercury levels (mainly methylmercury) are of more interest than total mercury, because methylmercury is much more toxic and may affect the central nervous system of consumers (Merian, 1991). However, for this study it was decided that costly organic mercury analysis would be performed only on fish samples which contained total mercury concentrations close to or exceeding the 0.5 mg kg^{-1} Canadian Guidelines. This strategy is a reasonable one since organic mercury comprises 80-95% of total mercury in fish muscle tissue (Bloom, 1992; May et. al., 1987; Westöö, 1967 and 1973; WHO, 1990). Since no fish contained high mercury levels, organic mercury analysis was not performed on any samples.

Table 3. Summary of total mercury and organic mercury concentrations in fish muscle tissue (wet weight) from the Red Deer River below the Dickson Dam sampled in 1983*

Species	Sample Size	Fork Length (cm)		Weight (kg)		Organic Mercury (mg kg^{-1})		Total Mercury (mg kg^{-1})	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
Walleye†	10	42.8	34.1-62.4	0.88	0.44-2.47	0.635	0.342-0.875	0.656	0.352-0.906
Northern Pike	6	49.6	36.7-73.2	1.17	0.39-3.37	0.301	0.168-0.468	0.310	0.115-0.480
Sauger‡	10	39.1	30.1-56.4	0.61	0.32-1.02	0.560	0.361-1.054	0.581	0.375-1.082
Lake Whitefish	5	29.9	17.1-41.1	0.50	0.08-1.11	-	-	0.119	0.038-0.185
Goldeye§	4	36.4	34.2-38.7	0.68	0.58-0.80	0.248	0.178-0.405	0.264	0.189-0.431
Northern Redhorse sucker**	2	40.8	40.5-41.0	0.96	0.88-1.04	-	-	0.485	0.472-0.497
Longnose sucker	2	42.5	42.2-42.8	1.19	1.17-1.20	-	-	0.179	0.148-0.209
White sucker	5	36.1	22.1-46.0	1.01	0.60-1.38	0.233	0.148-0.322	0.245	0.194-0.332
Burbot	5	56.6	49.5-60.2	1.08	0.81-1.25	0.243	0.137-0.389	0.256	0.147-0.417

* Data extracted with permission from Table 6 in Alberta Environmental Centre, 1984.
† Scientific name: Stizostedion vitreum
‡ Scientific name: Stizostedion canadense
§ Scientific name: Hiodon alosoides
** Scientific name: Moxostoma macrolepidotum

Table 4. Summary of total mercury and organic mercury concentrations in fish muscle tissue (wet weight) from Pine and Gleniffer lakes sampled in 1984*

Lake	Species	Year	Sample Size	Fork Length (cm)		Weight (kg)		Organic Mercury (mg kg^{-1})		Total Mercury (mg kg^{-1})	
				Mean	Range	Mean	Range	Mean	Range	Mean	Range
Pine	Northern Pike	1984	6	57.8	46.0-82.0	2.103	0.800-5.204	0.201	0.060-0.376	0.276	0.153-0.460
Gleniffer	Rocky Mountain Whitefish†	1984	20	22.6	16.4-31.6	0.133	0.053-0.388	0.133	0.037-0.248	0.166	0.076-0.286
	Burbot	1984	11	46.6	23.5-57.0	0.717	0.067-1.135	0.231	0.146-0.339	0.269	0.176-0.376
	Longnose Sucker	1984	20	34.0	21.1-38.9	0.567	0.126-0.816	0.155	0.065-0.285	0.187	0.090-0.357
	Northern Pike	1984	20	49.9	43.5-55.0	1.115	0.643-1.670	0.242	0.143-0.405	0.278	0.189-0.449
	White Sucker	1984	20	32.5	26.2-39.9	0.528	0.244-0.970	0.096	0.026-0.157	0.137	0.091-0.187
	All Species	1984	91	36.2	16.4-57.0	0.602	0.053-1.670	0.165	0.026-0.405	0.201	0.076-0.449

* Data extracted with permission from Appendix VI and XXI in Alberta Environmental Centre, 1986.

† Scientific name: Prosopium williamsoni

Table 5. Comparison of mean value of total mercury concentrations in northern pike muscle tissue in nearby aquatic systems

Site	Year	Sample Size	Fork Length (cm)		Weight (kg)		Total Mercury (mg kg^{-1})	
			Mean	Range	Mean	Range	Mean	Range
Red Deer River below Dickson Dam	1983	6	49.6	36.7-73.2	1.17	0.39-3.37	0.310	0.115-0.480
Gleniffer Lake	1984	20	49.9	43.5-55.0	1.115	0.643-1.670	0.278	0.189-0.449
Pine Lake	1984	6	57.8	46.0-82.0	2.103	0.800-5.204	0.276	0.153-0.460
The Narrows in Parlby Creek-Buffalo Lake	1993	15	46.2	38.6-52.9	0.781	0.493-1.231	0.164	0.079-0.269
			49.6†				0.186*	
			49.9†				0.189*	
			57.8†				0.249*	

* Derived from regression equation presented in Fig. 2(A) using a selected mean fork length value.

† Assumed mean fork length value equivalent to that in the other sites.

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Appendix A. Mercury Concentrations in Fish Muscle Tissues From The Narrows in Parlby Creek-Buffalo Lake

Sample Number		Species	Sex	Fork Length (cm)		Weight (kg)		Age (Year)	Total Mercury (mg kg^{-1})
Field	Lab			Field	Lab	Field	Lab		
11	9303760	Northern Pike	female	44.0	43.6	0.685	0.665	3	0.170
12	9303759	Northern Pike	male	51.4	51.1	1.030	1.007	5	0.225
13	9303761	Northern Pike	male	41.0	41.2	0.545	0.552	3	0.132
14	9303762	Northern Pike	female	50.9	50.7	0.945	0.925	5	0.178
15	9303758	Northern Pike	male	44.1	43.6	0.695	0.684	3	0.079
16	9303766	Northern Pike	female	50.6	50.1	0.950	0.838	3	0.177
17	9303765	Northern Pike	male	53.2	52.9	1.250	1.231	4	0.185
18	9303764	Northern Pike	male	47.4	46.6	0.900	0.793	4	0.161
19	9303763	Northern Pike	male	38.9	38.6	0.500	0.493	3	0.105
20	9303767	Northern Pike	male	49.8	48.8	0.890	0.870	6	0.269
21	9303770	Northern Pike	male	46.8	46.4	0.775	0.761	3	0.193
22	9303771	Northern Pike	female	46.6	46.3	0.770	0.758	5	0.219
23	9303772	Northern Pike	female	52.2	51.5	1.130	1.125	6	0.158
24	9303769	Northern Pike	male	42.2	41.2	0.535	0.519	3	0.104
25	9303768	Northern Pike	male	40.8	40.0	0.500	0.498	3	0.105
NA	9303754	White Sucker		-	35.5	-	0.676	-	0.077
NA	9303755	Longnose Sucker		-	41.7	-	0.997	-	0.089
NA	9303756	Longnose Sucker		-	40.8	-	1.035	-	0.109
NA	9303757	Longnose Sucker		-	41.2	-	1.100	-	0.114

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